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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No. : 09/991,287
Applicant : Richard W. Strobel
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Examiner : John J. Zimmerman

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DECLARATION

I, RICHARD W. STROBEL, hereby declare:

(1) That I am the sole inventor of the invention set forth in U.S. Patent Application Serial No. 09/991,287, filed November 14, 2001, and am familiar with the contents of said application;

(2) That I have reviewed the office action mailed April 28, 2003 and the prior art references relied upon by the Examiner;

(3) That with regard to U.S. Patent No. 3,503,721, to Lupfer, I find this patent to be directed to a tin-silver eutectic solder which may have a silver content that can vary from about 2.0 to 10%. It is well known however that solders, such as those of Lupfer, have much lower hardnesses than coatings formed using the process of the present invention. For example, by going to the web site www.matweb.com, one can see that a 95% tin – 5% silver solder will have a hardness of 0.032 GPa. In comparison, a 95% tin – 5% silver coating formed in connection with the present invention will have a hardness of 0.36 GPa – an order of magnitude greater. The same would hold true for a 90% tin – 10% silver coating vs. a 90% tin – 10% silver solder and a 98% tin – 2% silver coating vs. a 98% tin – 2% solder coating. With regard to claim 39 in the above-captioned patent application, Lupfer fails to disclose the claimed temperature maintaining step. Articles which are dip soldered using Lupfer's molten solder bath are dip soldered at a temperature below 221 degrees Centigrade (428 degrees Fahrenheit);

Considered 9/3 9/6/03

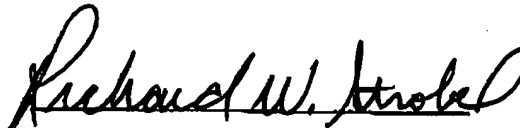
(4) That, U.S. Patent No. 5,075,176 to Brinkmann relates to an electrical connector pair with a male plug being given a tin alloy coating. The tin alloy coating may contain lead, as well as small amounts of deoxidization and processing additives and up to 10 wt% by weight of at least one element selected from the group consisting of silver, aluminum, silicon, copper, magnesium, iron, nickel, manganese, zinc, zirconium, antimony, rhodium, palladium, and platinum. There is nothing in the Brinkmann patent which would teach one of ordinary skill in the art to select silver from the laundry list of possible candidates and form a binary tin-silver coating system. If one looks at the examples in Brinkmann, the tin-silver alloy systems used by Brinkmann contain 4.0% or less silver in combination with phosphorous and/or other constituents. Phosphorous has a deleterious effect on hardness and electrical conductivity properties. To demonstrate this I had a test done at the Massachusetts Institute of Technology. The purpose of the test was to compare the hardness of a material having the same composition as Example 1 in the Brinkmann patent (namely, 99% Sn – 1% Ag – 0.03% P) with the hardness of samples having a composition of 98% Sn – 2% Ag, 95% Sn – 5% Ag, and 90% Sn – 10% Ag respectively. The test report is attached hereto as Exhibit A. As can be seen from FIG. 1B, materials having a coating with tin with a silver content in the range of 2% - 10% in accordance with the present invention have a hardness which is far greater than the hardness of the 99% Sn – 1% Ag – 0.03%P material. Further, the test shows that the hardness of the 99% Sn – 1% Ag – 0.03% P has a hardness far less than 0.32 GPa. With respect to electrical conductivity properties, the 99% Sn – 1% Ag – 0.03% P material has an electrical conductivity of 15.5% IACS. In comparison, coatings having a content of 98% Sn – 2% Ag, 95% Sn – 5% Ag, and 90% Sn – 10% Ag, have an electrical conductivity respectively of 16.0% IACS, 16.6% IACS, and 20.1% IACS;

(5) That U.S. Patent Nos. 5,902,472 to Arai et al. and 5,948,235 to Arai et al. are directed to tin-silver alloy plating solutions for forming an electrodeposited coating on a substrate. An electrodeposited coating is vastly different from a non-electroplated coating. In particular, electrodeposited or electroplated coatings are characterized by chemical bonds. Further, the inorganic compounds present in the electroplating bath are also present in the electroplated coatings. These inorganic compounds create resistance which lower the electrical conductivity of the coatings. Furthermore, electroplated coatings are characterized by deleterious undercuts and an inability to remain homogeneous. Non-electroplated coatings such

as those of the present invention do not suffer these problems. In fact, coatings formed using the process of the present invention have a cast structure; and

(6) That, in the process of the present invention, the substrate material is maintained within the coating bath for a time period in the range of 0.2 seconds to 10 seconds. This residence period is important in terms of form coatings having the hardnesses set forth in the claims of the application. Electroplating processes require longer ~~residence~~ ^{residence} times because as coating thickness increases, it takes longer to continue the deposition process. This is because more current is required.

The undersigned declares further that all statements made herein of his own knowledge is true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.


(Signature)

Date: 8-22-03

Objective

To use nanoindentation to determine the indentation hardness of a SnAg casting (99% Sn – 1% Ag – 0.03% P), and compare that indentation hardness to those samples tested in the same manner in August 2001.

Experimental Procedure

The casting was ground and polished to an 0.06 micron nominal surface roughness with a silica suspension, and tested shortly thereafter in a humidity controlled environment (<55% humidity). All experiments were conducted using a Hysitron Inc. TriboIndenter control system and Berkovich diamond indenter. Each indentation was imposed in (open loop) load control at a loading rate of 1 mN/s to a final load of 5 mN, resulting in a maximum depth of ~1000 nm. The first series of experiments consisted of 25 indentations, positioned as a 5x5 grid with 10 micron inter-indentation spacing. As the hardness calculated from these tests was significantly less than that calculated in August 2001, these tests were repeated in four additional positions on the same polished sample, with a 3 x 3 grid of 100 micron inter-indentation spacing at each position. This resulted in a total of 61 nanoindentation experiments on this sample, under identical testing conditions. Spurious data were eliminated and the entire data set was analyzed to calculate reduced Young's modulus E_r and indentation hardness (or average contact pressure) p_{avg} .

Data Analysis

Indentation data consists of simultaneously measured applied load P and resulting indentation depth into the sample h . This indentation P - h response can be analyzed by several published methods to calculate properties including hardness and Young's (elastic) modulus. These data were analyzed by the method of Oliver and Pharr.¹ Averages, standard deviation, and confidence factor (std dev/avg) of all of these calculations are reported below for values of indentation hardness p_{avg} and Young's modulus E_r .

Indentation hardness is calculated in units of pressure, and represents the average pressure which the sample can sustain beneath the indenter. Traditional hardness numbers such as Vickers hardness HV do not have physical units, and are not explicitly related to indentation hardness as calculated above. However, if one is more familiar with traditional hardness tests that report H as hardness, a rough relationship between these two values for the indenter geometry used here is:

$$H \sim 0.94p_{avg} \quad (1)$$

Results

The macrostructure visible in this casting after polishing showed significant heterogeneity, presumably due to segregation of Ag (dark) within a Sn matrix (light). For this reason, sets of indentations were positioned along the surface to sample regions of dense and sparse segregation. Table 1 shows the calculated values of E_r and p_{avg} as a function of position. Note that Position 5 is the data acquired in the initial experiment consisting of 25 indentations that sampled a 50 x 50 micron portion of the surface that was devoid of surface-visible segregation.

Figure 1a shows the variation of indentation hardness with position Figure 1b compares these values with those measured as a function of %Ag in August 2001. These earlier data followed a power law increase in p_{avg} with %Ag:

$$p_{avg} = 49(\%Ag)^{0.29} + 280 \text{ MPa} \quad (2)$$

This functionality would predict that 1%Ag would result in an approximate p_{avg} value of 329 MPa. However, the data from the present study indicate that an addition of 1%Ag and 0.03% P result in an average indentation hardness of 196 MPa +/- 20 MPa. This value is in fact 30% less than that measured for 100%Sn in August 2001.

The reason for this discrepancy may be due to some or all of three factors:

- (1) The tests of Aug. 2001 were not conducted in a controlled humidity environment and were provided ready for testing. Thus, there may have been a thin surface oxide present that contributed to increased hardness. The current tests occurred in a controlled humidity environment, and were conducted shortly after surface polishing, resulting perhaps in less surface oxidation. It should be noted, however, that the hardness measured in Aug. 2001 and in the current study are significantly greater than literature values of (Brinell) indentation hardness for 100% Sn (51 MPa).²
- (2) Although testing conditions were held constant, a different instrument was used in the current study. In Aug. 2001, I used a MicroMaterials NanoTest6000, but the current levels of vibration isolation of this instrument were insufficient for maximum indentation loads of 5 mN.
- (3) This result may be a real consequence of adding both Ag and P, and may reflect the considerable segregation visible on the casting surface. No significant difference in indentation hardness was measured in regions of dense and sparse segregation.

Calculated values of Young's modulus E were a weak function of position, averaging to a value of 75 GPa ($E_r = 80$ GPa). This value is 50% greater than the literature value for pure Sn (50 GPa)², but greater than that measured in Aug. 2001.

Table 1. Calculated values of reduced modulus and indentation hardness in SnAg casting

Position	E^* [GPa]	Std Dev	Error %	H [MPa]	Std Dev	Error %
1	72.85	11.20	15	244.97	0.04	16
2	90.82	2.80	3	170.61	0.01	5
3	85.82	6.20	7	166.40	0.02	14
4	80.57	2.63	3	202.15	0.01	3
5	80.04	5.63	7	195.75	0.01	8

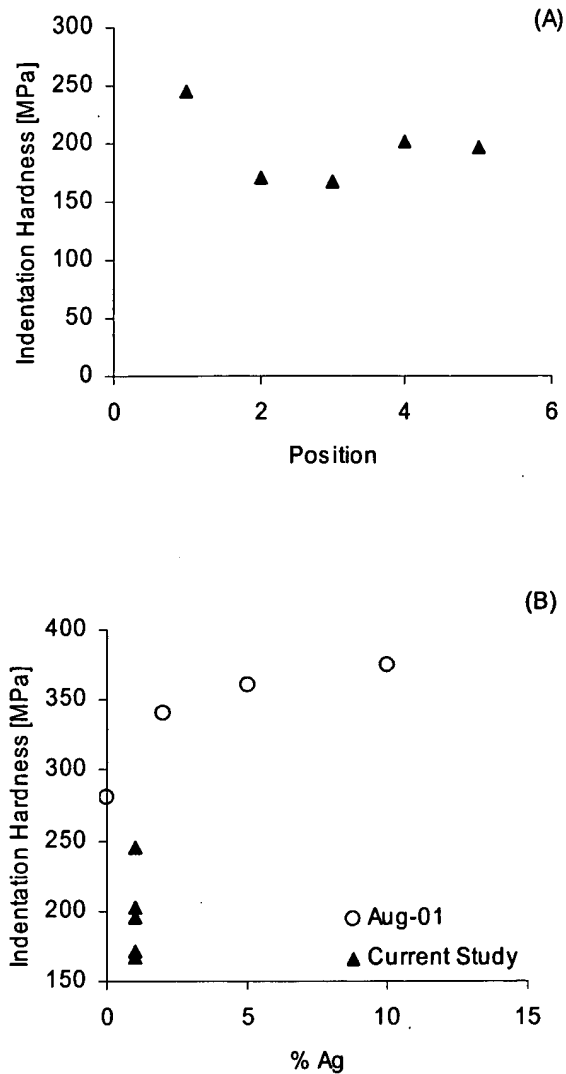


Figure 1. (A) Indentation hardness of Sn-based films as a function of position. Positions 1-4 are 3 x 3 grids of 100 micron spacing at points that reflect dense (Positions 2, 3) and sparse (Positions 1, 4) surface segregation. Position 5 is a 5 x 5 grid of indentations of 10 micron inter-indentation spacing, representing the preliminary experiment in a region that did not include surface segregation. (B) Indentation hardness in the current study as compared to that measured in August 2001 as a function of %Ag.

References

1. Oliver, W.C. and Pharr, G.M. "An improved technique for determination of hardness and elastic modulus using load and displacement sensing indentation experiments", *Journal of Materials Research*, Vol. 7, No. 6, June 1992.
2. <http://www.webelements.com/webelements/elements/text/Sn/phys.html>